FACTFILE:
GCE CHEMISTRY

A2 5.1 MASS SPECTROMETRY

Rewarding Learning

Learning Outcomes

Students should be able to:

5.1.1 recall the meaning of, and identify base peak, molecular ion peak, M+1 peak and fragmentation ions in a mass spectrum;

5.1.2 suggest formulae for the fragment ions in a given mass spectrum;

5.1.3 distinguish between molecules of the same RMM/mass using high resolution mass spectrometry;

In a mass spectrometer a molecule is bombarded by electrons and positive ions are formed. A molecular ion is formed by loss of one electron. This ion is detected in the recorder of the mass spectrometer, and a peak is printed on the spectrum.

$$M \longrightarrow M^+ + e^-$$

A molecular ion is an ion formed by the removal of an electron from a molecule.

A molecular ion peak is the peak produced by an ion formed by the removal of one electron from a molecule.

This peak has the highest value of m/e and it gives the relative molecular mass of the molecule. Sometimes there is a small peak 1 unit to the right of the molecular ion peak – this is called the M+1 peak. It has low abundance.

An M+1 peak is a peak produced by a molecular ion with an increased mass due to the presence of one carbon-13 atom.

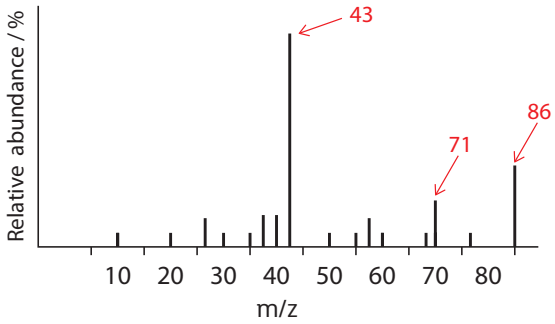
Other peaks are printed on the spectrum - this is due to bonds breaking in the molecule and the molecule breaking up, forming positively charged fragment ions which have different masses and so different peaks.

A fragmentation ion is a positively charged ion produced when the molecular ion breaks apart.

The base peak is the peak of greatest abundance in a mass spectrum.

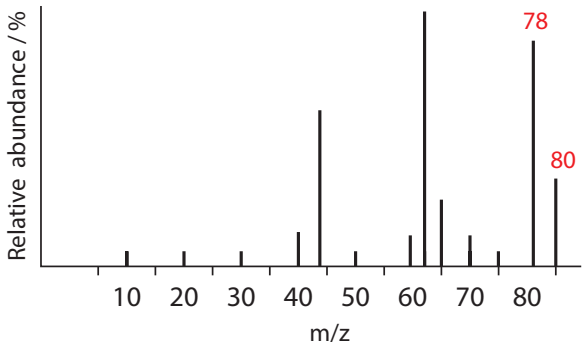
In a mass spectrum the y axis generally gives the abundance (usually %) – the more common a particular mass of a particle, the higher the abundance, and the higher the peak

The x axis gives the mass/charge ratio (m/e or m/z) – in a spectrometer the ions formed have a +1 charge, hence the m/e is the same as the mass.



The mass spectrum of pentan-2-one is shown above. The molecular ion peak is at 86 and the base peak is at 43. The other peaks are for fragment ions.

There are two molecular ion peaks in the mass spectra of compounds containing a single chlorine atom. This is because chlorine exists as two isotopes, ^{35}Cl and ^{37}Cl. The mass spectrum of 2-chloropropane, $CH_3CHClCH_3$, has a peak at m/z ratio 78 due to the molecular ion $[CH_3CH^{35}ClCH_3]^+$ containing an atom of ^{35}Cl. The peak at m/z relative abundance ratio 80 is due to the molecular ion $[CH_3CH^{37}ClCH_3]^+$ containing an atom of ^{37}Cl. The ratio of the peaks is 3:1. This ratio reflects the relative abundance of the chlorine isotopes; ^{35}Cl:^{37}Cl 3:1.



Mass spectrum of 2-chloropropane

High resolution mass spectrometry

Low resolution mass spectra give masses to the nearest whole number. High resolution mass spectrometry measures masses to 4 or 5 decimal places.

It can be used to distinguish between molecules. For example a low resolution mass spectrum which shows a molecular ion peak at 72, could be the mass spectrum for pentane, butanone or butanal, all of which have a relative molecular mass of 72. Using a high resolution mass spectrometer the molecular ion peak is at 72.0936.

A more accurate value of relative molecular mass of the molecular ions can be worked out using precise relative atomic masses, as shown below.

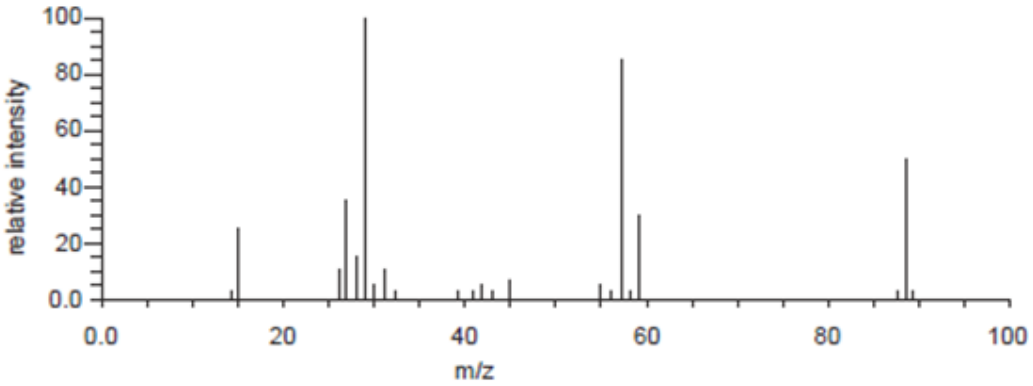
^{1}H= 1.0078
^{16}O= 15.9949
^{12}C= 12.0000

	formula	Accurate rmm
pentane	C_5H_{12}	72.0936
butanone	$CH_3COCH_2CH_3$	72.0573
butanal	$CH_3CH_2CH_2CHO$	72.0573

The molecular ion peak indicates that the molecule is pentane.

Revision Questions

1 The mass spectrum for methyl propanoate, $CH_3CH_2COOCH_3$, is shown below.



(i) What is the m/z value of the base peak?

..... [1]

(ii) Suggest the formulae of the species responsible for the peaks at 31 and 57.

31.....

57..... [2]

(iii) Explain why there is a peak at 89.

.....

..... [1]

2 Oxygen has three isotopes, ^{16}O, ^{17}O and ^{18}O. A sample was oxygen was analysed in a mass spectrometer and three groups of peaks were obtained.

group P corresponding to the ion O_2^+

group Q corresponding to the ion O^{2+}

group R corresponding to the ion O^+

Which one of the following is the order on the mass/charge axis, from left to right, of the groups?

A) P Q R

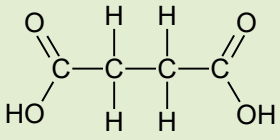
B) P R Q

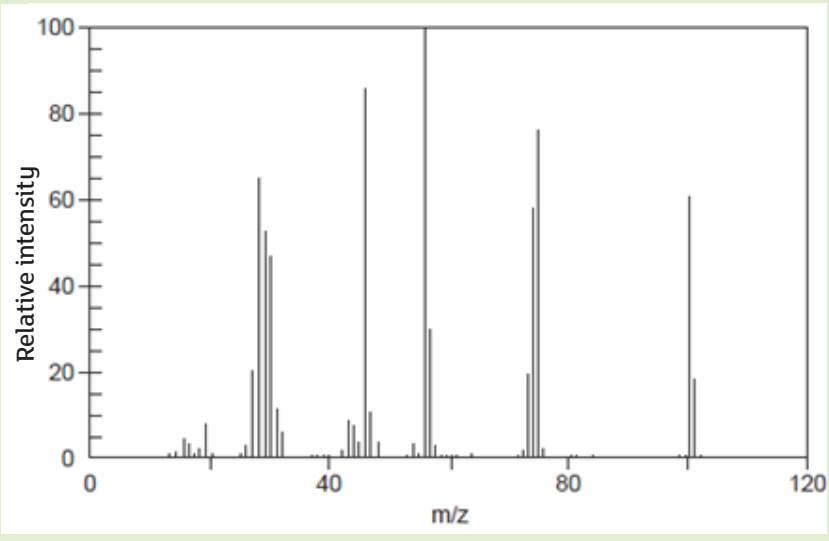
C) Q P R

D) Q R P

[1]

3 The structure and mass spectrum of succinic acid are shown below.





i) Explain the term **base peak.**

.....

..... [1]

ii) Identify the base peak.

..... [1]

iii) Suggest formulae for the following m/z values of the fragment ions.

45 ..... [1]

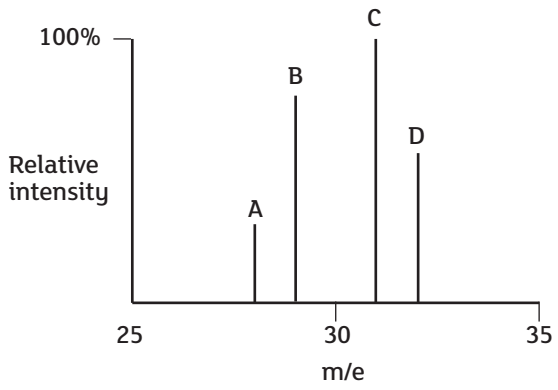
100 ..... [1]

4 Chlorine has two isotopes, chlorine-35 and chlorine-37.

Which one of the following is the number of peaks found in the mass spectrum of chlorine gas?

A	2
B	3
C	4
D	5

5 The mass spectrum of methanol is shown below. Which one of the following is the base peak?



[1]